

## ELECTROLYTIC DISSOCIATION IN SULPHURIC ACID AS STUDIED BY RAMAN EFFECT \*

By N. RAJESWARA RAO, M.Sc.  
Andhra University, Waltair

(Received for publication, April 18, 1940)

**ABSTRACT.** The Raman spectrum of sulphuric acid and its salts at different concentrations is studied, and the changes, with dilution, in the intensity of the lines observed in the spectra are made use of to study the electrolytic dissociation of the acid. An observation made by I. R. Rao and C. S. Rao, that the alkali salts are completely dissociated even in concentrated solutions, is made use of to calculate the absolute degree of dissociation of the acid. On calculating the number of dissociated and undissociated molecules in solutions of the acid and  $\text{KHSO}_4$ , it is observed that (1) the rate of dissociation of the acid is less in dilute solutions than in moderately concentrated solutions, (2) in equimolecular solutions of sulphuric acid and acid sulphate the dissociation of  $\text{HSO}_4$  molecules is larger in acid sulphate than in the acid. The above results are explained as due to the fact that in the solutions of the acid there is a larger abundance of  $\text{H}^+$  ions, than in the acid salt which therefore favours the formation of more  $\text{HSO}_4$  ions, in the acid.

### INTRODUCTION

The Raman spectra of sulphuric acid has been studied by a large number of workers including Nisi,<sup>1</sup> Woodward and Horner,<sup>2</sup> Ramakrishna Rao,<sup>3</sup> Bell and Jeppson,<sup>4</sup> Angus and Leckie<sup>5</sup> and Koteswaram.<sup>6</sup> The changes observed in the Raman spectrum of the acid on dilution are taken to be due to successive dissociation of the acid into  $\text{HSO}_4^+$  and  $\text{SO}_4^{++}$  ions, on lines similar to the explanation given by Ramakrishna Rao<sup>7</sup> in the case of nitric acid. But, nobody made a quantitative estimation of the degree of dissociation of this acid, as the spectrum was superposed by an intense continuum which masked the Raman lines to a large extent and made the determination of the intensities of the lines quite uncertain. The present work is undertaken with the purpose of making a quantitative study of the dissociation of the acid and its salts in aqueous solutions.

Woodward and Horner<sup>2</sup> observed that the continuous spectrum of the acid increases on diluting it to a certain extent and on further dilution it diminishes in intensity. They explained that this increase is due to the formation of

\* Communicated by the Indian Physical Society.

complex molecules which excite a continuous Raman spectrum. Medard<sup>8</sup> observed that the continuous spectrum could be diminished to a large extent by heating the acid with a few crystals of  $\text{KMnO}_4$ . Koteswaram<sup>9</sup> observed that this could be achieved by employing any oxidising agent,  $\text{K}_2\text{Cr}_2\text{O}_7$  or nitric acid, or by mere heating to about  $200^\circ\text{C}$ . The acid employed in the present work was treated with about 10 c.c. of pure nitric acid for about 200 c.c. of the pure acid and heated to about  $200^\circ\text{C}$  for about half an hour. With this sample, the author found absolutely no evidence for the increase in the continuous spectrum in the intermediate dilutions, reported by Woodward and Horner.<sup>2</sup>

#### EXPERIMENTAL

Solutions of the acid at various concentrations, and of  $\text{KHSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$  are prepared, using the same sample of conductivity water for all the solutions.  $\text{KHSO}_4$  is purified by repeated crystallisation, and  $(\text{NH}_4)_2\text{SO}_4$  is prepared by taking the pure sample of sulphuric acid and passing  $\text{NH}_3$  gas into it. The gas is made to pass through a tube packed with cotton in order to eliminate dust. Solutions of  $\text{KHSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  of the same molal concentrations are taken.

The arrangement for photographing the Raman spectra is essentially the same as that used by Ramakrishna Rao,<sup>7</sup> with some modification. It consists of a brass jacket which is rectangular in shape and has two cylinders of length 3 cm. and diameter just larger than that of the Wood's tube. The Wood's tube is passed through the cylinders and made water-tight by rubber washers. The box is open at the top, and the cooling water entering it by a narrow tube at the bottom passes over the Wood's tube and flows out by a wide outlet tube soldered at a corner throughout the height of the jacket. The mercury arc is placed right above the Wood's tube and in the space between the arc and the tube, there is sufficient layer of water to cool the Wood's tube from the heat radiated by the arc. The scattered light, after passing through a metallic tube which is blackened inside to avoid reflections on the walls of the tube, is focussed by means of an achromatic lens on to the slit of a spectrograph which has a high dispersion and good light-gathering power.

For the determination of relative intensities of the Raman lines, the spectra are taken with the different concentrations of the acid under identical conditions, in respect of the distance between the mercury arc and Wood's tube, the temperature of the liquid, the running voltage and current and the disposition of the arrangement for focussing the scattered light with respect to the slit of the spectrograph. The time of exposure for each of the solutions was exactly 5 hours. Thus, the changes in the intensity of the Raman lines from one concentration to another are due only to changes in the concentration of the acid and to changes in the nature of the molecular species arising

out of dilution, but not due to any external factors. The intensities of the lines are determined in the usual manner by taking a number of density marks with a Zeiss step-filter, on the same plate on which the Raman spectra are taken.

The process is repeated for the series of spectra obtained with solutions of  $\text{KHSO}_4$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{H}_2\text{SO}_4$  all having 3 gram-molecules per 1000 c.c. of solution. As the solution of  $\text{KHSO}_4$  gives a large continuum, a solution of  $\text{NaNO}_2$  is used as a filter to cut off radiations beyond 4358 towards ultraviolet. For this purpose the Wood's tube with a jacket containing the filter is used. Everytime the solution is changed the filter is also replaced afresh as it may undergo photochemical decomposition during the exposure, which is of 8 hours' duration for these three solutions.

#### RAMAN LINES IN SULPHURIC ACID AND THEIR ORIGIN

A characteristic feature of this acid is that all its Raman lines are broad, diffuse and bright. Hence, it is very difficult to locate the maxima of the bands exactly by micrometric measurement. That is the reason why the values of the frequencies given by various authors are found to differ. In such cases a microphotometric curve will be very useful in locating the positions of the maxima and the limits of the bands.

The assignment of the lines in the spectrum of sulphuric acid was made on the basis of the changes that they undergo on dilution. Ramakrishna Rao<sup>3</sup> found that the 1043-line increases in intensity on dilution and hence attributed it to  $\text{HSO}_4'$  formed on dilution as it is also found with considerable intensity in solutions of  $\text{KHSO}_4$ . The 980-line which appears in higher dilutions and also in solutions of sulphates is attributed to  $\text{SO}_4''$ . The lines 1171 and 1365, which could not be attributed to any radical containing  $\text{SO}_4''$  ion, but which were found to be analogous to similar lines with  $\text{SO}_2$  solution were attributed to molecules of the type  $\text{SO}_2(\text{OH})_2$ . The 910 line which decreases in intensity on dilution is due to undissociated  $\text{H}_2\text{SO}_4$  molecules. The bands 416 and 562 are of composite nature having a number of maxima and their variation in intensity with dilutions is irregular. So it is concluded that they are excited by all the three types of radicals, viz.,  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4'$  and  $\text{SO}_4''$ .

#### THE INTENSITIES OF THE RAMAN LINES

There are only three lines in the spectrum of sulphuric acid with Raman frequencies 910, 980, and 1043, for which the determination of the intensity is possible. These are as pointed out in the previous section excited by  $\text{H}_2\text{SO}_4$ ,  $\text{SO}_4''$  and  $\text{HSO}_4'$  respectively. The other lines are either too feeble, or are superposed by lines excited by the different types of molecules. So it is

considered that no useful purpose is served by determining their intensities.

Now, since the width of the lines 910 and 1043 is varying with dilution of the acid, the intensity of the maximum does not represent the intensity of the line. Curves are therefore drawn taking the intensity of the band at each point as ordinate and wave-number at the point as abscissa. The area of the curve is taken as a true measure of the intensity of the band.

Though Raman and Venkateswaran<sup>9</sup> announced recently that they have reason to believe that the Raman scattering is, to some extent at least, coherent, and that they are conducting some experiments which are expected to throw more light on the subject, it is generally accepted that the Raman scattering is incoherent. The intensity of the light scattered by a medium is therefore proportional to the number of molecules contained in it. Then the intensities of the lines excited by  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4'$  and  $\text{SO}_4''$  in solutions of various concentrations will be respectively proportional to the number of these molecules in the different concentrations. In the case of solutions of nitric acid, Ramakrishna Rao<sup>7</sup> suggested that if ' $n_c$ ' is the number of  $\text{NO}_3'$  ions at concentration ' $c$ ' and ' $n_o$ ' that at infinite dilution  $c_o$  then  $\alpha$ , the degree of dissociation is given by

$$\alpha = \frac{n_c}{c} \bigg/ \frac{n_o}{c_o}$$

and since  $n$  is proportional to the intensity  $I$ ,

$$\alpha = \frac{I_c}{c} \bigg/ \frac{I_o}{c_o}$$

But, with dilute solutions, very long exposures are required to obtain lines of measurable intensity. Therefore, by this method, it is possible to calculate only the degree of dissociation relative to one of the concentrations.

In a later publication, Ramakrishna Rao and C. S. Rao,<sup>10</sup> after studying a large number of strong electrolytes in aqueous solutions, arrived at the following results:

1. The salts of alkali elements dissociate completely at all concentrations.
2. The acid salts of the alkali elements dissociate completely as far as the alkali radical is concerned and the acid radical dissociates progressively.
3. Halogen acids, *viz.*,  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ , dissociate completely at all concentrations.
4. Oxy-acids dissociate progressively on dilution.

The first two results can be made use of to calculate the absolute degree of dissociation of sulphuric acid. Instead of taking an infinitely dilute solution to

calculate  $\frac{I_o}{c_o}$ , the solution of a salt having the same acid radical can be taken and the intensity of the line excited by the acid radical determined. If  $c'$  is the concentration of this solution, then  $\frac{I_o}{c_o} = \frac{I_{o'}}{c'}$ , since in both the cases, there is complete dissociation.

In fact, the intensity of radiation excited by each ion can be calculated, by determining the intensity of the line excited by the ion and dividing this by the total number of ions. This is specially useful, in calculating the degree of dissociation in a solution of a polybasic acid, for example, sulphuric acid taken up in the present work. By measuring the intensity of the  $SO_4''$  line in the spectrum of the solution of  $(NH_4)_2SO_4$ , the intensity of radiation excited by  $1N$   $SO_4''$  ions, where  $N$  represents the Avagadro number, is determined. Then, the intensities of the lines due to  $HSO_4'$  and  $SO_4''$  in the solution of  $KHSO_4$  are measured, and, by dividing the intensity of the  $SO_4''$  line in this spectrum by the intensity of radiation excited by  $1N$   $SO_4''$  ions calculated above, the number of  $SO_4$  ions in the  $KHSO_4$  solution is calculated. By subtracting this number from the total

TABLE I

Concentration of the solution in gm. moles per 1000 c. c.	Intensity of 910-line.	Equivalent intensity of 910-line	No. of $H_2SO_4$ molecules in gm. moles.		Intensity of 1013-line.	Equivalent intensity.	No. of $HSO_4'$ ions	Intensity of 980-line.	Equivalent intensity.	No. of $SO_4''$ ions	Percentage degree of dissociation of $H_2SO_4$ molecules.
			1	2							
16.9	2330	2330	15.7	15.7	860	860	1.2	—	—	—	7.1
14.9	1700	1035	13.0	14.0	1800	2046	2.9	—	—	—	17.2
12.8	1150	1518	10.2	10.5	3120	4120	6.5	—	—	—	38.2
10.8	765	954	6.3	6.7	1350	6839	9.8	11.8	18.5	0.4	60.3
8.7	—	—	—	4.2	4412	8375	11.9	15.2	29.5	0.6	74.1
6.8	—	—	—	3.2	3678	10570	13.1	13.0	32.6	0.7	85.3
3.0	—	—	—	1.1	1800	9223	15.0	6.5	36.6	0.8	93.3
$(NH_4)_2SO_4$ 3 gm. moles.	—	—	—	—	—	—	—	140.5	790.9	16.9	100
$KHSO_4$ 3 gm. moles.	—	—	—	—	1890	10647	15.7	8.7	49.0	1.2	100

number of  $\text{KHSO}_4$  molecules, the number of  $\text{HSO}_4'$  ions present is determined. Knowing the intensity of the line excited by  $\text{HSO}_4'$  ions in this solution and the number of undissociated  $\text{HSO}_4'$  ions as calculated above, the intensity of radiation excited by 1N  $\text{HSO}_4'$  ions is calculated. Now, knowing the intensities of the radiations excited by each of  $\text{HSO}_4'$  and  $\text{SO}_4''$  ions and knowing the intensities of the lines in solutions of sulphuric acid excited by these ions, the number of  $\text{HSO}_4'$  and  $\text{SO}_4''$  molecules in these solutions are determined. Dividing these numbers by the total number of molecules, the degrees of dissociation are calculated.

#### INTENSITIES AND DEGREE OF DISSOCIATION OF $\text{H}_2\text{SO}_4$ MOLECULES INTO $\text{HSO}_4'$ AND $\text{SO}_4''$ IONS

In the above table, the first column gives the concentration in gram-molecules of the acid in 1000 c.c. of the solution. In the second column the intensities of the lines of Raman frequency 910, corresponding to each concentration, are given. If there were no dissociation of the acid, the intensity of this line must be proportional to the concentration, as the times of exposure are equal. Thus, if with different concentrations the times of exposure were inversely proportional to the concentration, the intensities ought to be equal. To arrive at an idea as to how far there is dissociation of the acid, intensity of this line, as it ought to be if the times of exposures were inversely proportional to concentration, are calculated and given in column 3. From the values of the intensity in column 3, the number of undissociated  $\text{H}_2\text{SO}_4$  in gram-moles per 1000 c.c. of the solution, is calculated by the method indicated in the previous paragraph, and given in the first sub-column of column 4. For concentrations less than 10.75 gm.-molecules, the intensity of this line is too feeble to permit of quantitative determination. In the next sub-column is given the number of  $\text{H}_2\text{SO}_4$  molecules obtained by subtracting the number of  $\text{HSO}_4'$  and  $\text{SO}_4''$  ions from the total number of molecules. The closeness with which the values in these two columns agree indicate the validity of these calculations, and the validity of the conclusions drawn by I. R. Rao and C. S. Rao<sup>10</sup> regarding the dissociation in the salt solutions. The next three columns give the corresponding values for  $\text{HSO}_4'$  ions, and the next three for  $\text{SO}_4''$  ions. The 11th column gives the proportion of the dissociated  $\text{H}_2\text{SO}_4$  molecules to the undissociated which is the ratio of the sum of  $\text{HSO}_4'$  and  $\text{SO}_4''$  ions to the total number of molecules.

#### DISCUSSION OF RESULTS

The following main points are to be clearly noticed in calculating the numbers of the  $\text{H}_2\text{SO}_4$ ,  $\text{HSO}_4'$  and  $\text{SO}_4''$  radicals in solutions of the acid,  $\text{KHSO}_4$  and  $(\text{NH}_4)_2\text{SO}_4$ .

1. As the concentration of the solution is decreased, the number of  $\text{H}_2\text{SO}_4$  molecules becomes smaller and the number of  $\text{HSO}_4'$  molecules increases. This merely indicates that the  $\text{H}_2\text{SO}_4$  molecules are dissociated into  $\text{HSO}_4'$  ions in dilute solutions.

2. The rate of fall of  $\text{H}_2\text{SO}_4$  molecules or the rate of increase of the  $\text{HSO}_4'$  ions is large in moderately concentrated solutions, but in dilute solutions the rate is less as is evidenced by the Figs. I and II, where the curves are steep at moderate concentrations and as the dilution is increasing they get flattened.

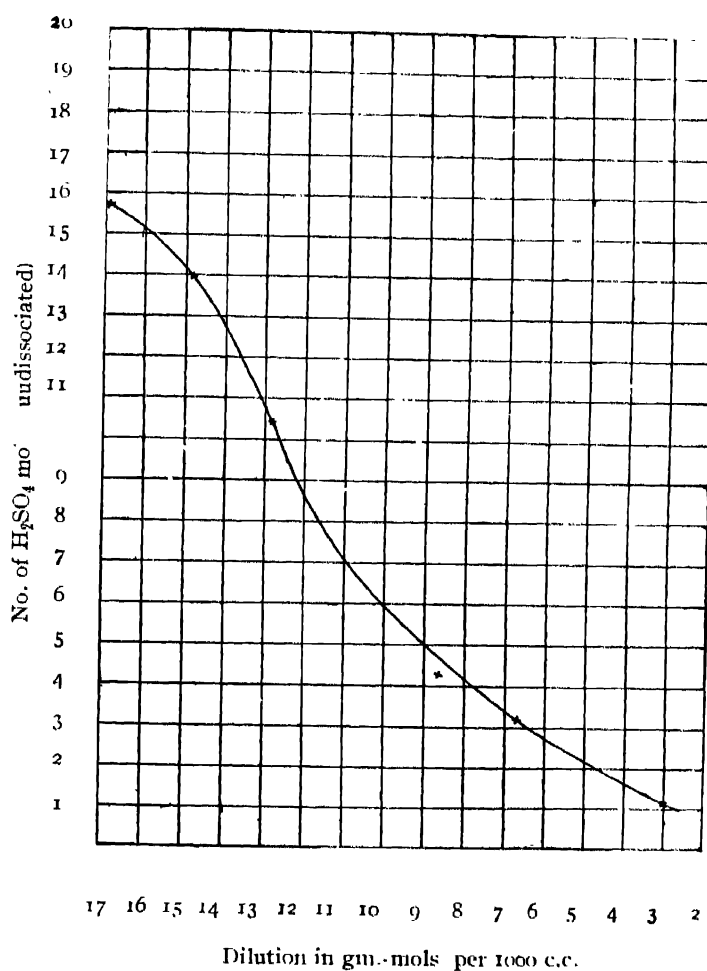


FIGURE I

The decrease in the rate of formation of  $\text{HSO}_4'$  ions in dilute solutions might be explained as due to their further dissociation into  $\text{SO}_4''$  ions. But the decrease in the rate of fall of the number of  $\text{H}_2\text{SO}_4$  molecules indicates that the

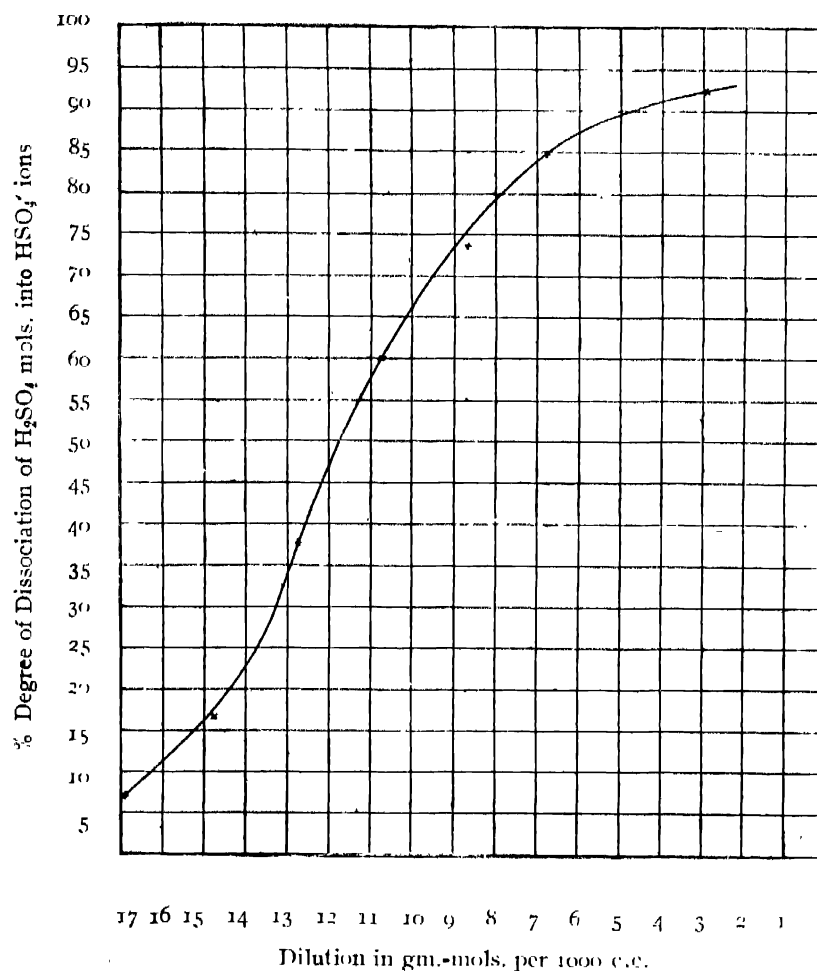


FIGURE 2

rate of dissociation is less in these solutions. This is further supported by the fact that the number of  $\text{SO}_4''$  ions is very small even in dilute solutions, which means that the dissociation of  $\text{HSO}_4'$  into  $\text{SO}_4''$  ions is very small.

This can be easily seen from the consideration that the equations



and



are reversible. As the dilution is increased, the number of  $\text{H}^+$  ions increases and hence the reverse action is more favoured. That is why, even at the concentration of 3 gram-moles per 1000 c.c., there is a considerable number of  $\text{H}_2\text{SO}_4$  molecules.

3. But in the case of the solution of  $\text{KHSO}_4$ , the dissociation of  $\text{HSO}_4'$  into  $\text{H}^+$  and  $\text{SO}_4''$  is larger than in an equivalent solution of the acid. This



is because the number of  $H^+$  ions is less in this solution than in that of the acid, where  $H^+$  ions are produced by both the reactions, whereas in the solution of the acid salt the reaction represented by (1) is absent.

4. The number of  $SO_4^{''}$  ions in the solution of  $(NH_4)_2SO_4$ , which assumed to dissociate completely is much larger than in the equimolecular solution of  $H_2SO_4$  or  $KHSO_4$ , as is expected, in view of the above considerations.

5. The above results state that the molecules in solutions of the acid or of the acid salt are not completely dissociated even in solutions of the order worked with in the present investigation. This means that the postulate of Debye and Hückel that in dilute solutions all strong electrolytes completely dissociate is not applicable to these dilutions. They do not contemplate any sub-classes in strong electrolytes, acids, salts, alkalis or acid salts. In very dilute solutions where there is complete dissociation, such classification is not necessary, but, for concentrations dealt with here, such classification is necessary as pointed out by I. R. Rao and C. S. Rao.

The author finds great pleasure in thanking Dr. I. Ramakrishna Rao under whose direction the present work is undertaken.

#### R E F E R E N C E S

- <sup>1</sup> Nisi, *Jap. J. Phys.*, **5**, 119 (1932).
- <sup>2</sup> Woodward and Horner, *Proc. Roy. Soc., A*, **144**, 129 (1934).
- <sup>3</sup> Rao, I. R., *Ind. Journ. Phys.*, **8**, 123 (1933).
- <sup>4</sup> Bell and Jeppson, *J. Chem. Phys.*, **2**, 711 (1934).
- <sup>5</sup> Angus and Leckie, *Proc. Roy. Soc.*, **149**, 327 (1935).
- <sup>6</sup> Koteswaram, P., *Ind. Journ. Phys.*, **12**, 299 (1938).
- <sup>7</sup> Rao, I. R., *Proc. Roy. Soc., (Amsterdam)*, **33**, 632 (1930).
- <sup>8</sup> Medard, *Compt. Ren*, **197**, 582 (1933).
- <sup>9</sup> Raman, C. V. and Venkateswaran, C. S., *Nature*, Dec. (1938).
- <sup>10</sup> I. R. Rao and C. S. Rao, *Nature*, April (1936).